PATENT
H0001160

ENVIRONMENTAL AND THERMAL BARRIER COATING FOR CERAMIC COMPONENTS

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Express Mail" mailing label number EL445861289US

Date of Deposit 11/21/01
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Environmental and Thermal Barrier Coating for Ceramic Components

CROSS REFERENCE TO RELATED APPLICATONS

[0001] This application claims the benefit of U. S. Provisional Application Serial No. 60/278,102, filed March 23, 2001.

BACKGROUND

[0002] The present invention relates to protective coatings for ceramic materials.

[0003] Advanced turbomachines use silicon (Si)-based ceramics such as silicon nitride, silicon carbide, and their composites for hot-section components. Due to the high temperature capability of Si-based ceramics, those ceramic turbomachines operate at higher temperatures with minimum cooling and higher engine performance. However, at operating temperatures above 1200°C, the Si-based ceramics can be adversely affected by oxidation and water vapor present in the flow stream. Such a hostile engine environment results in rapid recession of Si-based ceramics parts.

[0004] U.S. Patent 6,159,553 discloses the use of tantalum oxide (Ta_2O_5) as coating material on silicon nitride parts. A tantalum oxide coating of 2 to 500 microns in thickness can effectively protect the surface of silicon nitride parts from oxidation and reacting with water vapor at high temperatures. However, there are some limitations on pure tantalum oxide coating on Si-based parts:

1. Ta_2O_5 undergoes a phase transformation from low temperature phase (beta - phase) to high temperature phase (alpha-phase) at about 1350°C, which may cause cracking in the coating due to the volume change occurred during the phase transformation.
2. Ta_2O_5 is susceptible to grain growth at temperatures above 1200°C.

Pronounced grain growth results in large grain microstructure, which reduces the mechanical strength of the coating and induces high local residual stresses in the coating, and causes the coating to spall off.

3. Ta_2O_5 has a coefficient of thermal expansion (CTE) about 3×10^{-6} °C^{-1}, whereas silicon nitride has a CTE in the range of 3 - 4 x 10^{-6} °C^{-1} and silicon carbide (SiC) has a CTE in the range of 4 - 5 x 10^{-6} °C^{-1}. Since there is about 10 to 30% CTE mismatch between Ta_2O_5 and silicon nitride, and an even higher CTE mismatch between Ta_2O_5 and silicon carbide, residual stresses will develop in the Ta_2O_5 coating on Si-based ceramics. The residual stresses can limit the service life of the coating.

4. A pure Ta_2O_5 coating has low fracture toughness, which may adversely affect the mechanical integrity and the lifetime of the coating during service due to foreign object impact and particulate erosion events.

[0005] With those limitations, a Ta_2O_5 coating on Si-based ceramics would not provide adequate protection for turbine engine applications in which the maximum temperature goes above 1350°C, thousands of thermal cycles occur, and greater than five thousand (5000) hour coating lifetime is required. It would be highly desirable to significantly improve the Ta_2O_5 coating to meet those stringent demands for advanced ceramic turbine engine applications.

SUMMARY

[0006] According to one aspect of the present invention, a component comprises a silicon-based substrate; and a protective coating for the substrate. The protective coating includes tantalum oxide (Ta_2O_5) and an additive for suppressing transformation from beta Ta_2O_5 to alpha Ta_2O_5.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 illustrates a first method of improving the crystalline structure of a coating composition.

[0008] Figure 2 illustrates a second method of improving the crystalline structure of a coating composition.

[0009] Figure 3 is a schematic view of component formed in accordance with the present invention.

DETAILED DESCRIPTION

[0010] The present invention relates to Ta_2O_5-based coatings which can effectively protect Si-based ceramic turbine engine parts even when repeatedly subjected to extreme temperatures during operation. The coating compositions have improved microstructural and high temperature stability as compared to pure Ta_2O_5 when utilized to protect Si-based ceramic parts in turbine engine applications.

[0011] Applicants have found that the grain growth rate of Ta_2O_5 is reduced by the addition of alumina at temperatures above 1400°C. It is believed that the Al_2O_3 solid solution in Ta_2O_5 changes the defect structure of Ta_2O_5 such that ionic diffusion rate is slowed and that the transformation of beta to alpha Ta_2O_5, which triggers exaggerated grain growth at temperatures greater than 1350°C, is suppressed by the presence of Al_2O_3.

[0012] Applicants have found that the sintering property of Ta_2O_5 is also

improved with the addition of alumina. Pressed pellets containing between 1.0 to about 10 mol% of Al_2O_3 have shown noticeably higher density than pure Ta_2O_5 pellets sintered under the same condition. This improved sinterability is believed to be due to the reduction of Ta_2O_5 grain coarsening rate by the Al_2O_3 addition, and/or the enhancement of Ta ion lattice diffusion as the number of cation vacancies is increased by the diffusion kinetics due to the presence of Al ions.

[0013] The solid solubility of Al_2O_3 in Ta_2O_5 may be about 10 mol % at about 1500°C. Since alpha-Al_2O_3 has a CTE about 8 x 10^{-6} °C^{-1}, the CTE of a 10 mol% Al_2O_3-90 mol% Ta_2O_5 alloy would be about 3.5 x 10^{-6} °C^{-1}, which is 10% higher than the pure Ta_2O_5 and closer to the CTE of silicon nitride. When the amount of Al_2O_3 in Ta_2O_5 exceeds about 10mol %, a second phase having the formula of $AlTaO_4$ forms that has a CTE about 5 x 10^{-6} °C^{-1}. As the alloy composition increases to 25 mol% Al_2O_3 – 75 mol% Ta_2O_5, the microstructure includes a mixture of Ta_2O_5-Al_2O_3 solid solution and the $AlTaO_4$ compound, and the CTE is about 4 x 10^{-6} °C^{-1}, which matches well with that of SiC. If the Al_2O_3 concentration exceeds 25 mol%, the CTE of the coating would become too high for application on Si_3N_4 substrate. For SiC and its composites having CTE in the range of 4 - 5 x 10^{-6} °C^{-1}, the Ta_2O_5 coating can incorporate up to 50 mol % Al_2O_3 so that the majority of the phase in the coating becomes $AlTaO_4$ and the CTE match very well with the substrate.

[0014] A variety of ceramic processing methods can be used to introduce and incorporate the additives into Ta_2O_5. As shown by the method 100 in Figure 1, the process may start with a commercially available Ta_2O_5 powder (step 102), to which a desirable amount (about 1 – 50 mol.%) of additives are added (step 105). The additives or their precursors can be in the form of powders that require only simple (either dry or wet) mixing with the Ta_2O_5 powder (step 106). After mixing (and drying, if wet mixing in a liquid medium is performed) the mixture 120 is ready for coating operation 108. Optionally, the mixture is subject to calcination (step 110) in

which the mixture is heat-treated to a temperature up to 1600°C, after which with or without milling or grinding (step 112), before the coating operation. Coating is then performed (step 108), as described below.

[0015] Referring to Figure 2, an alternative method 113 of applying the additives includes starting with precursor compounds (either solids or liquids) containing the additive ions (step 114). The precursor compounds are dissolved in a solvent such as water or an alcohol 116 (step 116), mixed with Ta_2O_5 powder (step 118), (alternatively, the Ta_2O_5 powder can be dispersed in the solvent first, and added with the precursors), and then precipitated onto the surface of the Ta_2O_5 particles (step 120). After drying (step 122), calcination (step 122), and/or milling/grinding (step 124), the mixture is then ready for the coating operation 126.

[0016] The coating operation (step108, 126) for applying the mixture created by either of the methods 100 or 113 may include plasma spray, sol gel, and chemical vapor deposition. Moreover, the coating can be formed by sintering pressed ingots or similar components at about 1350°C for 1 to about 20 hours, and using Physical Vapor Deposition, (PVD) or Electron Beam Physical Vapor Deposition (EB-PVD) methods, the latter being well known in the field of thermal barrier coating on super alloy turbine engine parts. Both PVD and EB-PVD coatings have the benefit of forming a smooth surface, allowing strong bonding to the substrate, and uniform additive distribution.

[0017] The additive is not limited to an oxide of aluminum. The additive for the coating may include one or more of other oxides, compounds, or their precursors of Al, Hf, Si, Ln (rare earth including whole lanthanum series and Y) Mg, Mo, Ni, Nb, Sr, Ti, and/ or Zr. Those additives may affect the CTE of tantalum oxide, mostly shifting it higher. An additive such as La_2O_3 can induce an acicular-grain-shaped second phase having the formula $La_2Ta_{12}O_{33}$, and thereby produce a duplex microstructure that results in a strong material with high toughness. Additional

additives (e.g., nitrides, carbides, borides, silicides) can be introduced to further inhibit grain growth, modify CTE, and reinforce tantalum oxide. These additives result in lower grain growth, higher CTE and increased fracture toughness.

[0018] Figure 3 shows a component 200 formed in accordance with the present invention. Component 200 includes a substrate 202 which may be formed of Si-based material such as a SiC-SiC composite material. A thermal protective coating layer 204 is applied to the outer surface of substrate 202 as described above.

[0019] The coating layer 204 may be formed of a mixture of Ta_2O_5 and one or more additives including Al_2O_3 or La_2O_3. The coating thickness can be accurately controlled by EB-PVD techniques and may vary between 0.5 to 10 mil.

[0020] During application, the additive(s) in the coating layer 204 may go into solid solution of form compounds with the tantalum oxide. Therefore, the amount of additive(s) in the finished component may be different than the amount of the starting material.

EXAMPLES

[0021] Example 1. Compositions having 1, 10 and 25 mol% Al_2O_3 as the additive to Ta_2O_5 were prepared. In each batch, about 1 Kg of a commercial beta Ta_2O_5 powder was mixed with commercial Al_2O_3 powder in isopropanol in a milling jar for about 2 hours before drying. After drying was complete, the powder was sieved to classify the particle size to about 5 to 100 micron range in preparation for plasma spray coating. If the particle size was too fine, a calcining process was included to coarsen the particles. A coating of the above composition was then applied to coupons of silicon nitride and SiC-SiC composite substrates by an air-plasma spraying process. The silicon nitride coupons had an as-sintered surface on which the plasma coating was applied. Alternatively, a grit-blasted machine surface

could have been utilized. The coupons were then degreased, and preheated to about 1000°C by either a torch or furnace. The powder was then fed into a high velocity, high temperature plasma air flow. The ceramic powder became molten and subsequently was quenched and solidified onto the coupons. The coating thickness varied from about 2 to about 10 mil, or about 50 to about 250 microns. The coated samples were then subjected to cyclic furnace testing wherein each sample was held in the furnace at about 1315°C for about 30 minutes, and then quickly removed from the furnace and quenched to about 200°C in a stream of blowing air. The silicon nitride coupons coated with Al_2O_3 in the range of about 1 to 25 mol% survived about 100 hours and 200 cycles without spalling. X-ray diffraction showed the Ta_2O_5 remained in the beta phase.

[0022] Example 2. Compositions having 3, 4, 6 and 10 mol% La_2O_3 as the additive to Ta_2O_5 were prepared. In each batch, about 1 Kg of a commercial beta Ta_2O_5 powder was mixed with commercial La_2O_3 powder in isopropanol in a milling jar for about 2 hours before drying. After drying was completed, the powder was sieved to classify the particle size to about 5 to 100 micron range in preparation for a plasma spray coating. The composition was applied to coupons of silicon nitride and SiC-SiC composite substrate by air-plasma spray process. The silicon nitride coupons had as-sintered surfaces on which the plasma coating was applied. Alternatively, a grit-blasted machine surface could have been utilized. The coupons were then degreased, and preheated to about 1000°C by either a torch or furnace. The powder was then fed into a high velocity, high temperature plasma air flow. The ceramic powder became molten and subsequently was quenched and solidified onto the coupons. The coating thickness varied from about 2 to about 10 mil, or about 50 to about 250 microns. The coated samples were then subjected to cyclic furnace testing wherein each sample was held in the furnace at 1315°C for about 30 minutes, and then quickly removed from the furnace and quenched to about 200°C by a stream of

blowing air. The silicon nitride samples coated with La_2O_3 in the range of 3 to 6 mol% survived more than 1000 hours and 2000 cycles at 1315°C. The SiC-SiC samples having La_2O_3 in the range with 4, 6 and 10 mol % survived more than 2,000hrs and 4,000 cycles. SEM examination showed needle-shaped $La_2O_3 - Ta_2O_5$ precipitates on the coating surface. X-ray diffraction showed the existence of a second phase containing La, possibly the $La_2Ta_{12}O_{33}$ phase according to the phase diagram. These needle-shaped second phases distributed uniformly throughout the coating increased the fracture toughness and mechanical strength of the coating. They also increased the CTE of the coating such that the CTE mismatch between the coating and the substrate was significantly reduced, resulting in improved coating life performance as shown by repeated heating during the cyclic furnace testing.

[0023] Example 3. The SiC-SiC coupon coating was prepared with a 50-mol% Al_2O_3 addition in the same manner as Example 1 which survived the same cycle furnace testing for over 100 hours without spalling. After the testing, the coating has transformed to the $AlTaO_4$ phase with some residual Ta_2O_5. Silicon nitride coating coupons having coating compositions of 10 mol% Al_2O_3-90 mol% Ta_2O_5 survived 500 hours at 1315°C and 1000 cycles without spalling. X-ray diffraction of the tested sample shows that the predominant phase in the coating remains the beta Ta_2O_5 with some $AlTaO_4$ phase.

[0024] Example 4. Two coating compositions, 1 mol% Al_2O_3-99 mol% Ta_2O_5 and 5 mol% Al_2O_3-95% Ta_2O_5, were heat-treated at 1450°C for 2 hours. X-ray diffraction showed that the samples remained predominantly beta Ta_2O_5 after the heat treatment. In contrast, pure beta Ta_2O_5 completely transformed to alpha Ta_2O_5 after a heat treatment of 1 hour at 1450°C. Scanning electron microscope examination showed that the grain size for the 5 mol% Al_2O_3 coating composition fired at 1450°C was significantly smaller than the pure Ta_2O_5 sample fired at the same temperature. The coating composition of 5 mol% Al_2O_3-95 mol% Ta_2O_5 was further heated at

1550°C for 15 hours, and the Ta_2O_5 remained as beta phase after the heat treatment.

[0025] Example 5. Powders of two compositions, 7.5 mol% Al_2O_3 –92.5 mol% Ta_2O_5 and 4 mol% La_2O_3-96 mol% Ta_2O_5, respectively, were pressed into cylindrically-shaped green parts and sintered at 1350°C for 10 hours to form ingots for EB-PVD coating. Substrates of silicon nitride and SiC-SiC composites were loaded in a vacuum chamber and an electron beam was focused on an ingot of the material to be deposited. The electron bombardment resulted in high local heating on the coating material, which evaporated atomistically and condensed onto the part. Oxygen gas was bled into the system to compensate for the loss of oxygen from Ta_2O_5 during the evaporation. The coating was chemically bonded to the substrate. The substrate was preheated to 800-1200°C to improve bonding with the deposited material. The coated silicon nitride and SiC-SiC parts having a 50 micron thick coating survived the above-described cyclic furnace testing at 1315°C for over 500 hours and 1000 cycles.

[0026] Although the present invention has been described above with reference to specific embodiments, it is not to be so limited. Instead, the present invention is to be construed according to the following claims.